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Polypyrrole Actuators: Properties and Initial Applications

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5.1 Summary

Polypyrrole actuators are low-voltage (1–3 V), moderate to large strain (2–35%), and relatively high stress (up to 34 MPa) actuator materials. Strain rates are moderate to low, reaching 11%/s, and frequency response can reach several hertz. Faster response (> 1 kHz) is anticipated in nanostructured materials. Forces can be maintained with minimal power expenditure. This chapter reports on the current status and some of the anticipated properties of conducting polymer actuators. Applications investigated to date include braille cells, shape changing stents, and variable camber foils. Situations where low voltage operation is valuable and volume or mass are constrained favor the use of conducting polymers.

Polypyrrole and other conducting polymers are typically electrochemically driven and can be constructed in linear or bending (bilayer) geometries. Synthesis can be by chemical or electrochemical means, and raw materials are generally very low in cost. These polymers are electronically conducting organic materials. They also allow ions to diffuse or migrate within them. An Increase in the voltage applied to a polymer electrode leads to removal of electrons and an increasingly positive charge within the volume of the polymer. This charge is balanced by negative ions that enter the polymer from a neighboring electrolyte phase (or by positive ions that leave). Ion insertion is generally accompanied by expansion of the polymer. The ions, solvent, and synthesis conditions determine the extent of this expansion, which can be anisotropic. A change in modulus has also been observed as a function of the oxidation state.

Models relating charge, strain, voltage, stress, and current have been developed that allow designers to evaluate the feasibility of designs. One of these modeling approaches is presented with the aim of enabling selection of appropriate device geometry.

The field of conducting polymer actuators is developing rapidly with larger strains, stresses, cycle lifetimes, and rates reported every year. The background needed to understand these developments and to decide if polypyrrole and in

general conducting polymer actuators are appropriate for use in a given application is provided.

5.2 Introduction and Overview

Conducting polymer actuators are relatively new, and applications are at an early stage of development. In this article, basic properties and models are presented, and a few example applications are given, in the hope that this information will guide and stimulate further applications. The introduction provides a general overview, following the format of a recent review article on electroactive polymers [1]. Many of the topics are discussed subsequently in more detail, including an overview of conducting polymer properties, a description of electrochemical synthesis of the polymers, and a brief overview of two basic device configurations. This is followed by a discussion of models that are intended to guide design.

Conducting polymers are electronically conducting organic materials featuring conjugated structures, as shown in Figure 5.1. Electrochemically changing the oxidation state leads to the addition or removal of charge from the polymer backbone, shown in Figure 5.2, and a flux of ions to balance charge. This ion flux, often accompanied by solvent, induces swelling or contraction of the material [2–8]. Insertion of ions and solvent between polymer chains likely induces the majority of the volume changes. Conformational changes in the backbone may also play a role. Changes in oxidation state and in dimension can also be chemically induced [6].

Important advantages relative to most other electroactive polymers are the high tensile strengths, which can exceed 100 MPa [9], and large peak stresses of up to 34 MPa [10]. The stiffness is also higher than in many electroactive polymers, with the modulus generally exceeding 0.1 GPa and often reaching ~ 1 GPa modulus [11–13]. Furthermore, the modulus can be a function of oxidation state, potentially enabling controllable stiffness [14]. A major advantage over piezoelectrics, electrostatic actuators, dielectric elastomers, and ferroelectric polymers is low voltage operation (~ 2 V), which is particularly useful in portable, battery-driven applications, and often enables the actuators to be driven without the need for extensive and costly voltage conversion circuitry. Initial work demonstrated only moderate strains of several percent – much greater than piezoceramics, but less than those observed in a number of other emerging actuation technologies [1]. Recent work has demonstrated that significantly larger strains can be obtained, in excess of 35% for a few cycles and routinely around 9% [15–17].

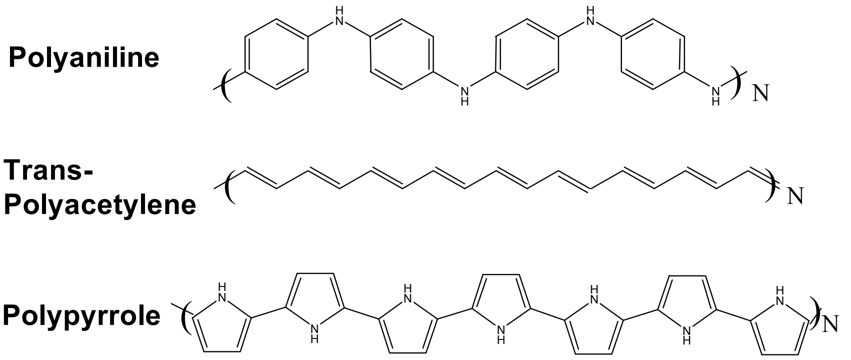


Figure 5.1. The chemical structures of some common conducting polymers employed as actuators

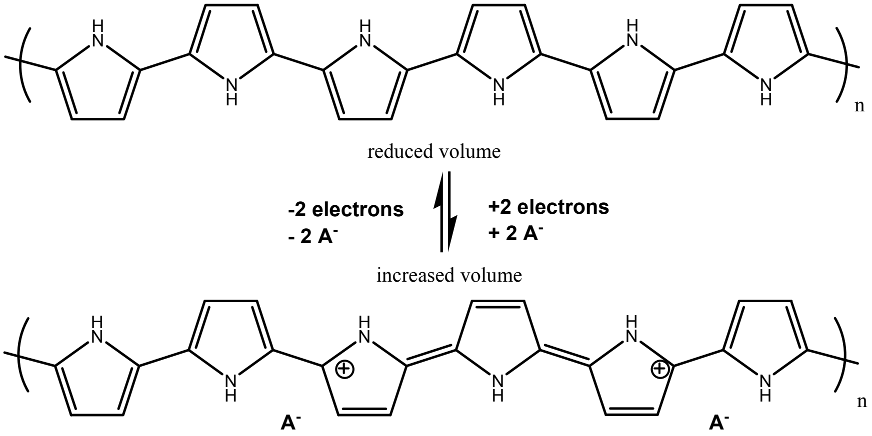


Figure 5.2. Electrochemical redox cycle for polypyrrole. A^- represent anions, e^- electrons. In general, the polymer expands when ions are inserted

The electromechanical coupling is generally less than 1%, except for small strains [18,19]. This means that only a small fraction of the input electrical energy is converted to mechanical work [1]. This does necessarily mean that the efficiency is low because much of the input electrical energy is stored and can be recovered. The principal impact is the need to shunt a lot of charge, as discussed below. This shunting can become an issue for the power supply in large devices. Encapsulation is often required to contain electrolyte, which is generally in the form of a liquid or gel. Strain rates are moderate (11%/s max to date [20]), but there is an opportunity for substantial improvement [18]. Rates are limited by internal resistance of the polymers and electrolytes and by mass transport rates of ions inside the polymer [18,21].

Experiments show that strain, ε, is proportional to the density of charge, ρ, transferred over a range of strains of about 1% or more:

$$\varepsilon = \frac{\sigma}{E} + \alpha \cdot \rho \tag{5.1}$$

where σ is the applied stress and E is the elastic modulus [4,9,11,18,19]. The strain to charge ratio, α, is approximately $\pm 1\text{–}5 \times 10^{-10}\ \mathrm{m^3 \cdot C^{-1}}$ [22]. The strain to charge ratio is negative when cations dominate the ion transfer and positive when anions serve to balance charge [5]. For larger strains, this relationship continues to hold to first order. When loads exceed several megapascals, creep and stress relaxation can be significant [10].

In some systems, the volume change observed appears to be close to the volume of ions inserted [22,23], but often this model of actuation is an oversimplification. For example, the polymer can exhibit gel-like behavior, where change in oxidation state is associated with large solvent flux, large volume changes, and significant changes in modulus [24].

Rate is determined by the speed at which charge can be injected. Current is restricted by the resistance of the cell (when electrochemically activated) and by the rate at which ions are transferred within the polymer [18,19,21]. Some of the internal resistance can be compensated for, leading to substantially faster rates, as discussed below [25]. The fastest response occurs in thin, highly conducting films [12]. Changes in oxidation state have been observed at kilohertz rates [26].

Table 5.1. Conducting polymer actuators. Adapted from [1].

Property	Min.	Typ.	Max.	Limit
Strain (%)	1	3–9	> 35	
Stress (MPa)		1–5	34	200
Work sensity (kJ/m^3)		70		1000
Strain rate (%/s)		1	11	10,000
Power (W/kg)			150	100,000
Life (cycles)		28,000	800,000	
Coupling			0.1	
Efficiency (%)		< 1	18	
Modulus (GPa)	0.1	0.8	3	
Tensile strength (MPa)		5	120	400
Applied potential (V)		1.2	10	
Charge transfer (C/m^3)	10^7		10^8	
Conductivity (S/m)		10,000	45,000	
Cost (US$/kg)	3		1000	

Polypyrrole and polyaniline are the most widely used conducting polymers, but actuation has also been demonstrated in polyacetylenes [3], polythiophenes, and polyethyldioxithiophene [27]. Starting materials are readily available (*e.g.*, www.aldrich.com, www.basf.com). Electrodeposition is commonly used [28], producing thin (~0.3–40 μm thick) films with typical widths of 10 mm and lengths up to 1 m or more. An example synthesis process for polypyrrole is described below. Samples may be electrodeposited as tubes [29], often with an ingrown conductor to improve conductivity and maximize rate. Chemical synthesis may also be used in polypyrrole and other conducting polymers [30–32]. The properties of the polymers are very dependent on the solvent and salts used in deposition and also the electrolyte employed during actuation [8,11,13,33–40]. For example the cycle life (for redox cycling at least, and potentially for actuation) can be extended to approximately one million cycles from several tens of thousands by using ionic liquid electrolytes [32].

Forces can reach tens of newtons with displacements of several millimeters, and mechanical amplification increases displacements up to about 100 mm [41]. Voltages of only 1–2 V are sufficient for activation, but higher voltages help speed the response by overcoming internal resistance [42]. Currents reach hundreds of milliamperes. When not moving current is minimal, even when forces are applied. In such a case, virtually no energy is expended, and the condition is known as a catch state. This state is particularly useful where actuation is intermittent because no power is dissipated during periods where the actuator is simply holding a load.

Response under conditions other than room temperature and pressure have received little attention. Conductivity and mass transport are expected to decrease in proportion to the square root of absolute temperature, affecting rates at low temperatures. Electrolyte freezing will drastically reduce rate. Typical freezing temperatures are between –60°C and 0°C. Creep may increase substantially with temperature.

Conducting polymers are well suited to low voltage, moderate to high force, and small length scale applications. For macroscopic applications to be effective, layers of thin porous films could enable extremely fast, high power response (> 100 kW/kg) [18]. Recovery of stored electrochemical energy should enable moderate efficiencies to be achieved even at full strain. Newly designed conducting polymers promise larger strains and higher electromechanical coupling but are still at an early stage of development [17,43–46].

Data and models valuable to engineering design of conducting polymer actuators, and particularly polypyrrole based actuators, are provided by Madden *et al.* [18,19] and Mazzoldi *et al.* [13], a discussion of current status, promise and remaining challenges is given by Smela *et al.* [47,48]. Some early work on applications including braille cells, variable camber hydrofoils, and actively steerable catheters are provided by Spinks [49], Madden *et al.* [41,50] and De Rossi [51], respectively.

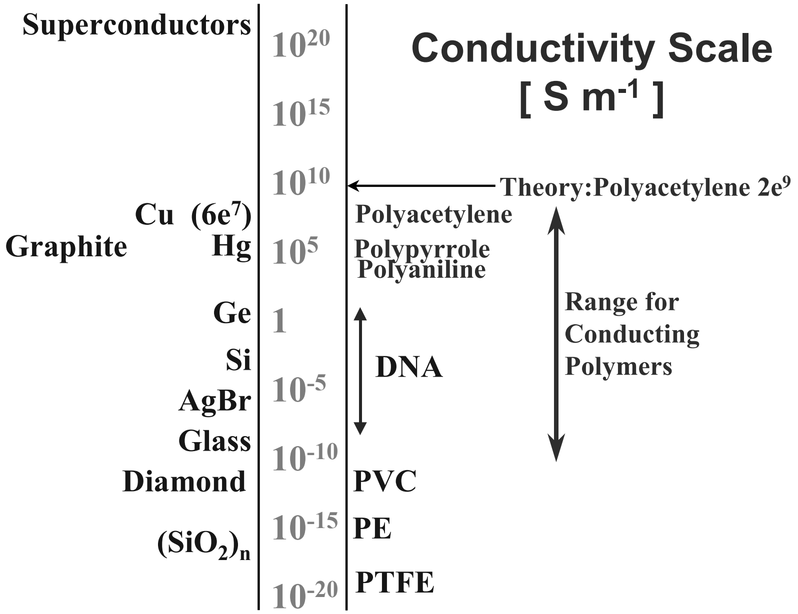


Figure 5.3. Conductivities of conducting polymers relative to other common polymers and inorganic materials. PE is polyethylene, PVC is polyvinylchloride, and PTFE is polytetrafluoroethylene, also known as Teflon©. The upper limits in conductivity for the conducting polymers polyaninline, polypyrrole, and polyacetylene are shown. Adapted from H.-G.Elias, Mega Molecules. Berlin: Springer-Verlag; 1987 [52]

5.3 Polypyrrole and Conducting Polymers – Background

What are conducting polymers, and what other properties do they have that can be useful in robotics? This section defines conducting polymers based on their molecular structure and describes their electronic properties.

Conducting polymers exhibit electronic conductivity, making them unusual among organic materials, as depicted in Figure 5.3 [52,53]. A defining feature of conducting polymers is their conjugated backbone, seen in Figure 5.1, enabling some degree of electron delocalization and hence electronic conduction, akin to the electronic behavior in benzene and graphite [54].

The polymers shown in Figure 5.1 are semiconductors. Charge carriers must overcome a band gap to become delocalized and enable conduction [55]. The band gap in polyacetylene is 1.7 eV [56]. Conductivity decreases with temperature, as the number of carriers with sufficient thermal energy to reach the conduction band is reduced. The band gap is reduced in a process analogous to doping in crystalline semiconductors [56]. Doping involves the addition or removal of charges from the polymer chain, resulting in structural changes and the creation of states in the band gap. These changes in polymer oxidation state are generally performed chemically or electrochemically. In the chemical doping process, electrons or protons are effectively donated to or withdrawn from the polymer backbone via chemical reactions with dopant molecules. In electrochemical doping, the conducting polymer is in electrical contact with an electrode in an electrochemical cell, as shown in Figure 5.4. Electrons are added to or removed from the polymer via the electrode, thereby changing the oxidation state. The electrochemical oxidation process leads to a change in the polymer charge state, which is balanced by the flux of ions to or from the electrolyte. These ions are referred to as dopants.

Although the doping process is analogous to doping in silicon and other crystalline semiconductors, there are some notable differences. Doping levels in conducting polymers are much higher, reaching one dopant for every two or three monomer units on the polymer backbone. The dopant need not be a donor or an acceptor in conducting polymers, often it is present simply to maintain charge balance. Charge carriers in the polymer are not simply electrons or holes, but are coupled with local conformational distortions in the polymer chain, among other differences [57]. In the doped state, conductivities can be appreciable, as shown in Figure 5.3.

In general, doping is chemically or electrochemically reversible. Conductivity can be switched by up to 13 orders of magnitude, an effect used in electrochemical transistors [58]. Reversible doping is used in many applications including batteries, electrochromic devices, supercapacitors, and chemical sensors, as well as being associated with volume change. The dimensional changes are used to perform mechanical work, as shown in Figure 5.4. Thus, actuation in conducting polymers is derived from dimensional changes associated with changes in the polymer oxidation state.

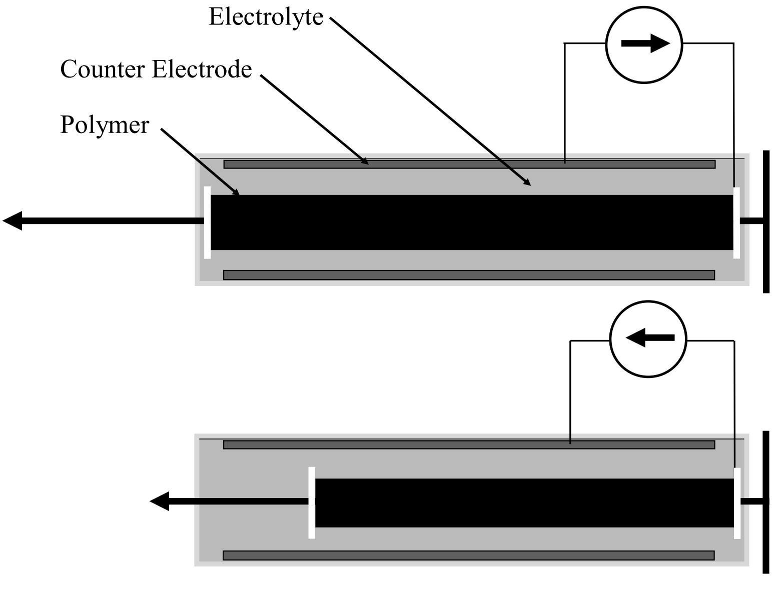


Figure 5.4. Electrochemical oxidation and reduction of polypyrrole. An electrochemical cell is depicted, showing the basic elements required. Current is applied leading to either oxidation or reduction of the polymer and a corresponding expansion or contraction

Conducting polymers are extremely versatile materials which have been employed to make high energy density storage devices, sensors, gas filters, generators, computational elements, display technologies, conductive wires, strong fibers, and actuators [57]. This diversity, combined with techniques for processing and patterning, make conceivable the fabrication of entire, multifunctional, and autonomous devices from a single material, as is currently being done with silicon microelectromechanical systems. Conducting polymers have a number of advantages over silicon, including much higher energy storage capability and an actuator technology that is superior in a number of respects. For example, the capacitance of > 100 F/g in polypyrrole [59, 60] is about five orders of magnitude higher than that achieved on the surface of silicon. The polymer actuators operate at low voltages, unlike the piezoelectrics and electrostatic actuators used in silicon microelectromechanical systems, offer much higher work densities than electrostatics, and ten or more times the strain offered by piezoceramics [61].

In conducting polymers, actuation is the result of molecular level interactions. The ability to tailor material properties by molecular design creates the potential to rationally design polymers that will achieve required mechanical properties. Ultimately, it may be possible to develop molecular stepping motors akin to muscle. Steps towards this goal are already being taken [1,62,63]. This article focuses on the current performance of conducting polymer actuators. This is a rapidly developing field however, in which performance limits are continually being pushed to new limits.

5.4 Synthesis

Properties of conducting polymer actuators are critically dependent on synthesis conditions. All polypyrrole actuators and many others reported in the literature are electrochemically synthesized, and thus an example electrodeposition proceedure is presented here. Electrochemical synthesis leads to the highest conductivity and the best mechanical properties in polypyrrole. It is also the most accessible method to nonchemists. The method presented leads to very conductive and high tensile strength films and requires only readily available solvents, salts, and monomers. A source of current is all the instrumentation required. The amount of material deposited depends only on time and current.

In this commonly used method, films are grown as summarized in Figure 5.5. A solution of 0.06 M freshly distilled pyrrole monomer (Aldrich, Milwaukee, WI, USA, www.aldrich.com) and 0.05 M tetraethylammonium hexafluorophosphate (Aldrich) in propylene carbonate is employed, following the procedure of Yamaura and colleagues [28]. The pyrrole monomer need not be distilled, but the conductivity and mechanical proerties are greatly improved by purification. If distillation is not available, the pyrrole monomer, which is a liquid at room temperature, can be purified by passing it through activated alumina or stirring in alumina powder and then removing the powder using a filter. Polypyrrole is deposited galvanostatically (constant current) onto polished glassy carbon substrates (Alfa Aesar, Ward Hill, MA, USA, www.alfaaesar.com) at current densities of between 1 and 2 $A \cdot m^{-2}$, resulting in a film thickness between 8 and 100 µm, depending on time. Other substrates can be used, including platinum, gold, and stainless steel. When using gold or stainless steel, it is found that thicker films can lift off the mandrel during electrodeposition, leading to films that look bubbled or warped. This liftoff may be reduced by employing a roughened surface. A copper counterelectrode is used. For best results, deposition should take place at temperatures between –30°C and –45°C in a nitrogen saturated solution. The resulting films have conductivities between 20 and 45 $kS{\cdot}m^{-1}$, densities of 1500 to 1800 $kg{\cdot}m^{-3}$ dry, and tensile strengths that can exceed 100 MPa.

The polished glassy carbon substrates take the form of either 100 mm × 100 mm × 1 mm thick plates, or a crucible. The crucible is employed to obtain films that are up to 1.5 m in length, with a width of 4 mm. Figure 5.6 shows the crucible after deposition, including the Kapton© tape that is spirally wound to mask the surface so that a continuous film is electrodeposited. Also shown is a 1.3 m long film that has been removed from the crucible.

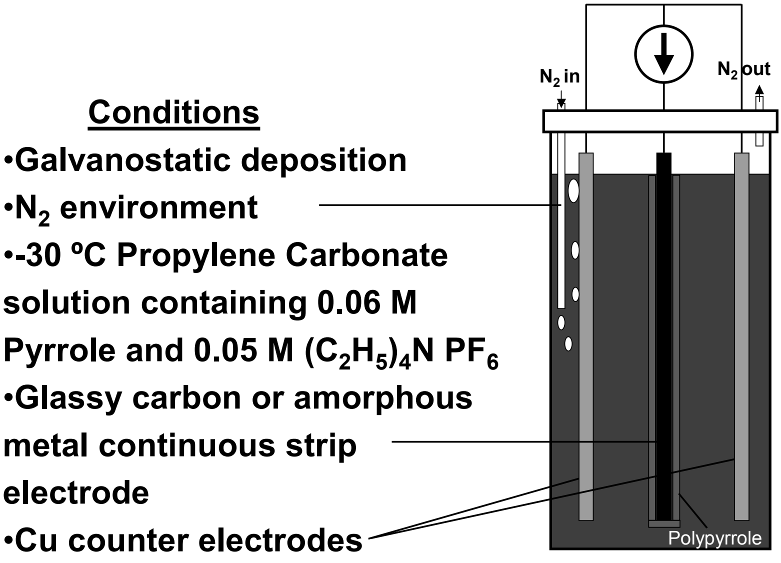


Figure 5.5. Polypyrrole synthesis conditions. The diagram summarizes the conditions used in the synthesis of the hexafluorophosphate doped polypyrrole films employed in this study

The reaction steps involved in electrochemical synthesis have been proposed by Baker and Reynolds [64] and are shown in Figure 5.7. It is not necessary to understand the synthesis steps, but it can help in analyzing failed depositions. When current density is too low, the solution is sometimes black, often indicating that only oligomers (short chains) have been formed. These short chains drift away from the electrode before they reach a the critical size for precipitation onto the electrode.

As synthesized, polypyrrole has a backbone configuration shown at the bottom of Figure 5.2, where roughly one-third of the monomers are charged [28,34,64-66]. The backbone charge is balanced by the presence of anions. In this state, polypyrrole is shiny black in appearance and has typical conductivities of up to ~10^4 S·m^{-1}, reaching 10^5 S·m^{-1} when stretch aligned [28]. Reduction leads to a semiconducting state, shown in Figure 5.1.

In bulk, the monomer costs ~US$1.00 per kilogram. The estimated minimum cost of electrodeposited polypyrrole is ~$1.50 per kilogram.

Variations on the method presented include growth on a platinum wire onto which a smaller wire is spirally wound [67]. The smaller wire is incorporated into the polypyrrole that is grown onto the larger wire, and the polypyrrole plus small wire are pulled off the larger wire following deposition. A key advantage of this approach is that the small wire increases electrical conductivity and hence, in many cases, the rate of actuation. It also allows the polymer to be taken deeper into its reduced (nonconducting) state, allowing larger actuation. In a variation of this approach, polymer is grown onto a spirally wound wire that does not have a core. This approach relies on the polymer growing between spiral windings but does not require removal of the large diameter wire.

Figure 5.6. Synthesis of long films on a crucible. At right is the glassy carbon crucible employed to electrodeposit polypyrrole films up to a meter in length. The crucible is masked using Kapton© tape, resulting in a film shown at left. Photos courtesy of Patrick Anquetil

The polypyrrole described typically produces strains in the 2–4% range. Larger strains can be obtained by varying deposition conditions. For example, Kaneto *et al.* showed a >10% strain by operating polypyrrole in an aqueous (water-based) solution of $NaPF_6$ [68], and larger strains have been claimed in other papers [16,44]. Spinks, Wallace, and others at the University of Wollongong and Santa Fe Science and Technology have shown that growth in propylene carbonate followed by redox cycling in ionic liquids can lead to increased cycle life, suggesting that it may be possible to increase the lifetime beyond 1 million cycles [32,69].

5.5 Actuator Configuations and Applications

Some applications require large forces, other large displacements, and sometimes a combination of both is needed. There are two common actuator configurations – linear actuators in which films or fibers contract or expand producing linear displacement, and bending actuators in which a bending motion is produced. The advantage of bending actuators is that they produce large displacements, but this is done at the expense of force. Linear actuators generate high forces – typically in the range of 1 to 10 MN per square meter of cross-sectional area–but their change in length can be relatively small – generally 1–10 % of the original length. In designing a device, the challenge is then to scale up the forces produced by bending actuators or scale up the displacements produced by linear actuators [41]. Bending actuators consist of two or more laminated films, as depicted in Figure 5.8. In the simplest case one of the films contracts leading to bending. If two sheets of polypyrrole are used, then one may expand while the other contracts. In this case, the sheets are separated by an ionically conductive medium.

The equations for the deflections and forces of bilayer and trilayer structures follows the same approach as is used in bimetallic strips [5]. For a trilayer in which both outer layers are active polymer of the same thickness and equal and opposite strain, separated by a passive layer, the equations for relative curvature, *K*, charge per unit volume, ρ, and force at the end of the beam, *F*, are [70]

$$F = C_{\text{spring}} \cdot K + C_{\text{charge}} \cdot \rho \tag{5.2}$$

where

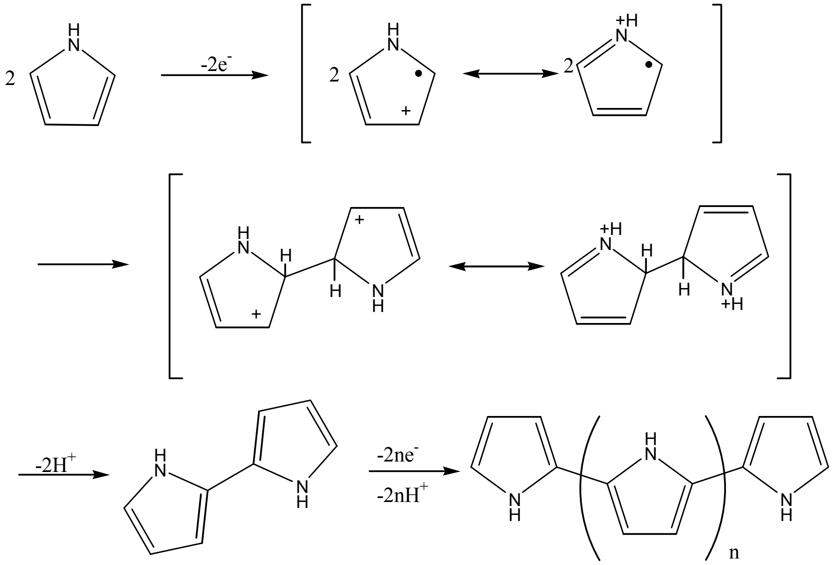
$$C_{\text{spring}} = \frac{2 \cdot W \cdot E_p}{3 \cdot L} \cdot h_g^3 \left[\left(1 + \frac{h_p}{h_g} \right)^3 - 1 + \frac{E_g}{E_p} \right] \tag{5.3}$$

and

$$C_{\text{charge}} = \frac{E_p \cdot \alpha}{L} \cdot W \cdot h_g^2 \left[\left(1 + \frac{h_p}{h_g} \right)^2 - 1 \right] \tag{5.4}$$

E_p and E_g are the moduli of elasticity of the active polymer and separators, respectively. H_p and h_g are the thicknesses of each layer, *W* and *L* are the width and legnth of the structure, and α is the linear relationship between strain and charge per unit volume, introduced in Eq. (5.1) above. Maximum force is generated when bending is prevented (K= 0), and peak deflection occurs when the applied force is zero (F= 0).

Synthesis of Polypyrrole



The last step is a in fact a repetion of the first steps beginning with oxidation, followed by coupling to either end of the polymer, and finally elimination of H^+. The electrons are either removed via an electrode (electrochemical deposition) or chemically, e.g.

$$\text{Fe+++} \xrightarrow{e^-} \text{Fe++}$$

Note that the polymerization does not generally result in a neutral polymer shown above, but rather the backbone is charged, as below, such that the total number of electrons transferred per monomer is 2+*a* where *a* is generally between 0.2 and 0.5:

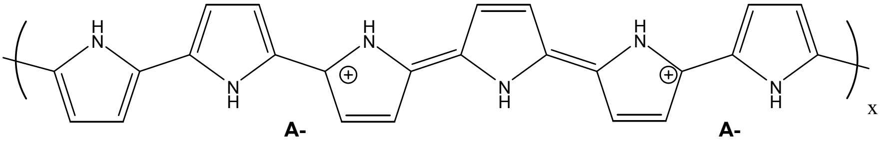


Figure 5.7. Mechanisms of Polypyrrole polymerization

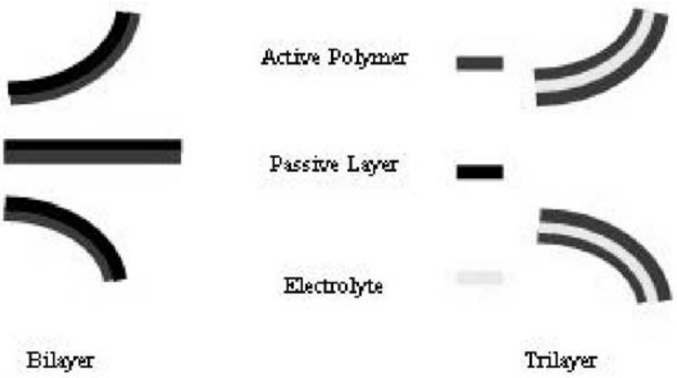


Figure 5.8. Bilayer and trilayer actuation configurations. In bending bilayers and trilayers, one layer expands whereas the other is passive or contracts, leading to a bending motion.

An example trilayer actuator is shown in Figure 5.9 [41]. It is employed to create a camber change in a propeller blade. The structure generates 0.15 N of force. Bilayers have been shown to be very effective for microscale actuation and have been used by Elisabeth Smela and her colleagues to create contracting fingers, cell enclosures, moveable pixels, and “micro-origami.” Micromuscle.com in Sweden is working to commercialize actuated stents and steerable catheters, which appear to use the bilayer principle for operation [51].

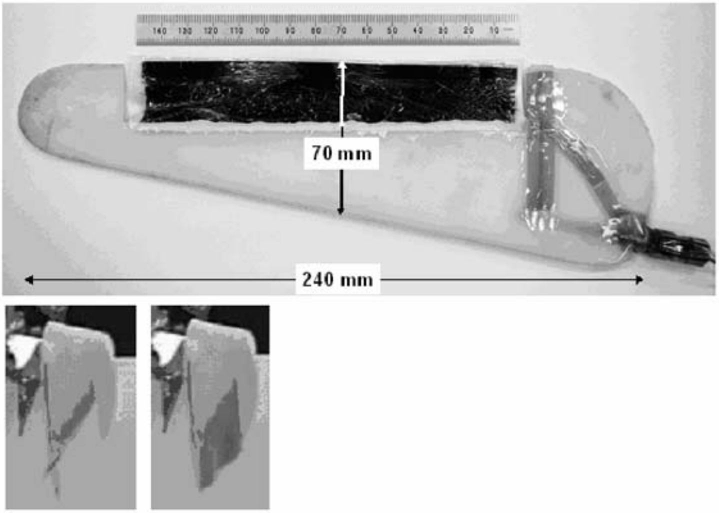


Figure 5.9. Trilayer acutator mounted on a propeller blade. The top image shows the geometry of the blade; the bottom two images show deflection of the structure. In the trilayers (black), two films of polypyrrole are separated by a sheet of paper soaked in gel electrolyte. A thin layer of polyethylene encapsulates the bending structure. © Journal of Oceanic Engineering, reproduced with permission [41].

Figure 5.4 shows the basic geometry of a linear actuator approach. As in all actuator configurations, a counterelectrode and an electrolyte are required. Generally, a mechanism must be available to allow transmitting force and displacement to the load. Thus, the counterelectrode, electrolyte, and any packaging must not significantly impede actuation. Also, the counterelectrode must accept a tremendous amount of charge from the polymer actuator, which stores charge within its volume with an effective capacitance of approximately 100 Farads per gram of polymer. The counterelectrode is best made of a polymer that can itself absorb a lot of charge without requiring a large voltage or degrading the electrolyte. One of the simplest solutions is to employ a conducting polymer counterelectrode.

In some cases with linear actuators, no amplification of strain is needed. One such application is the creation of braille cells for the blind. These tablets feature arrays of pins that must be actuated up or down in a pattern across a tablet so as to generate text and refresh once the reader has completed the page. A group at the University of Wollongong in collaboration with Quantum Technology of Australia is developing a braille display in which each pin is driven by a polypyrrole tube actuator [71]. The polypyrrole tube is grown on a platinum wire (~ 0.5 mm diameter) which has a smaller diameter wire wrapped around it (~ 50 μm). The polypyrrole with the small wire encapsulated in it is removed from the larger wire by sliding it free. This approach allows relatively long actuators to be produced which, when driven with large currents, have very little voltage drop along their length due to the incorporation of the platinum wire. Voltage drop needs to be prevented because a gradient in voltage leads to a different degree of strain as a function of length along the actuator. Sections of the actuator distant from the electrical contact points receive very little charge and produce negligible actuation when the resistance of the actuator is large. The spiral winding of the wire allows its mechanical stiffness to be low, minimally impeding the strain of the polypyrrole. The hollow core enables electrical and mechanical connection via a wire. Tensile strengths are not as high as in the freestanding films, but operation at several megapascals of stress is common.

Figure 5.10 shows an example of a linear-actuator-driven variable camber foil [41]. In this case, a lever mechanism is needed the 2% strain of the polypyrrole employed needs mechanical amplification by a factor of 25. The actuators shown produce 18 N of force, which is reduced to 0.7 N in the process of amplifying the displacement. The actuators are sheets of freestanding polypyrrole.

5.6 Modeling and Implications for Design

In this section, a model of the relationship between electrical input and mechanical output is presented and used to explore the advantages and limitations of conducting polymer actuators. The presentation is similar to that given elsewhere by the author [18,19]. In particular rate limiting factors are discussed, as well as factors that determine efficiency and power consumption. These considerations allow designers to determine the feasibility of employing conducting polymers in specific applications and then to generate designs.

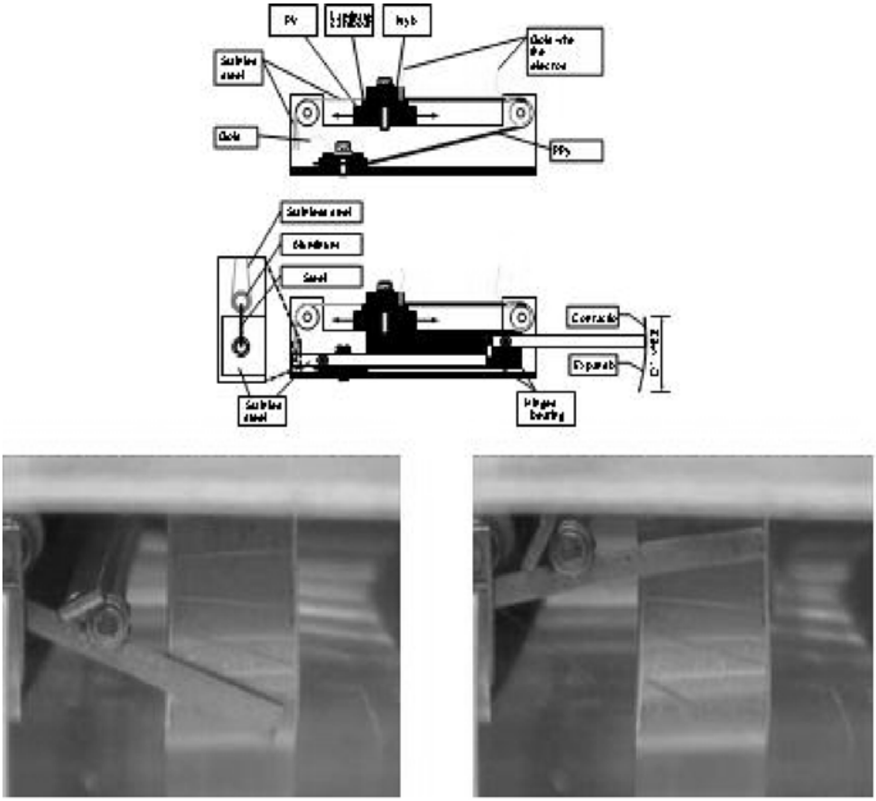


Figure 5.10. Linear-actuator-driven variable camber hydrofoil. The top image shows the actuator mechanism. The bottom images show the extent of deflection of the trailing edge of the foil. © Journal of Oceanic Engineering, reprinted with permission [41]

Equation (5.1), repeated again here, is a relatively simple relationship [19] between stress, σ, strain, ε and charge per unit volume, ρ as a function of time, t:

$$\varepsilon(t) = \alpha \cdot \rho(t) + \frac{\sigma(t)}{E} \tag{5.1}$$

which is found to describe the behavior of polypyrrole and polyaniline actuators to first order under a range of loads and potentials. In polypyrrole grown in PF_6^-, for example, if it is operated at loads of several megapascals and below and kept within a limited potential range (~ -0.6 V to +0.2 V vs. Ag/AgCl), this equation works resonably well. The strain to charge ratio, α, is analogous to a thermal expansion coefficient, but for charge rather than temperature. In conducting polymers, the strain to charge ratio is experimentally found to range from 0.3–5×10^{-10} $m^3 \cdot C^{-1}$ for polypyrrole and polyaniline actuators [9,13,19], and the modulus ranges between 0.1 and 3 GPa [12,13,72].

There are conditions under which Equation (5.1) does not apply. The model can be more generally expressed as

$$\varepsilon(t) = \alpha(t,V)\cdot\rho(t) + \frac{\sigma(t)}{E(t,V)} \tag{5.5}$$

E(t, V), the time and voltage dependent modulus [19,22]. The modulus has been found to exhibit both time and voltage dependence, showing a viscoelastic response at higher loads, for example [18]. When taken over large potential ranges, the modulus can change significantly, leading to increases or decreases in strain as load increases, depending on whether the change in modulus adds or subtracts from the active strain [3,72]. Over long time periods (> 1000 s) at high stresses (> 10 MPa), the modulus becomes highly history dependent [73]. Also, rate of creep can be enhanced during actuation [10]. The strain to charge ratio can be load independent, but frequency and time dependence have been observed [10]. The strain to charge ratio is particularly time dependent when more than one ion is mobile, a situation that is particularly difficult to model when both positive and negative ions move, simultaneously swelling and contracting the material [5]. The strain to charge ratio can also change as a function of voltage.

5.6.1 Relationship Between Voltage and Charge at Equilibrium

A complete electromechanical description includes input voltage in addition to strain, stress, and charge. In conducting polymers, the relationship between voltage and charge is difficult to model because the polymer acts as a metal at one extreme and an insulator at the other. A wide range of models have been proposed. In general, the response is somewhere between that of a capacitor and a battery [13,74–80]. In a capacitor, voltage and charge are proportional, whereas in an ideal battery, the potential remains constant until discharge is nearly complete. In oxidation states where conductivity is high, it is not unusual to find that charge is proportional to applied potential over a potential range that can exceed 1 V [18], thereby behaving like a capacitor [19,22,76,79–81]. In hexafluorophosphate-doped polypyrrole, this capacitance is found to be proportional to volume [22], and has a value of C_V=$1.3\cdot10^8$ F·m^{-3} [19]. At equilibrium, the strain may then be expressed as

$$\varepsilon(t) = \alpha\cdot C_V\cdot V + \frac{\sigma(t)}{E}, \tag{5.6}$$

where V is the potential applied to the polymer. In many conducting polymers and for extreme voltage excursions, the capacitive relationship between voltage and charge is not a particularly good approximation. These situations are difficult to model from first principles, so an empirical fit to a polynomial expansion in charge density may provide the most practical approach. The capacitative model is useful in evaluating rate-limiting factors even if the relationship between voltage and charge is complex. In such cases, the capacitance is determined by dividing the charge transferred by the voltage excursion. Before considering rate-limiting mechanisms, some considerations in choosing maximum actuator load are presented.

5.6.2 Position Control and Maximum Load

The designer must determine the stresses at which to operate an actuator. Conducting polymer actuators are able to actively contract at 34 Mpa [22,82]. In general, however load induces elastic deformation and creep [19,22,82–84]. To maintain position control, the actuator must be able to compensate for these effects. Over short periods, only the elastic response need be considered. The elastic strain induced by load is simply the ratio of the load induced stress, $\Delta\sigma$, and the elastic modulus, E. This strain must be less than or equal to the maximum active strain, $\varepsilon_{\max}$, for an actuator to maintain position:

$$\varepsilon_{\max} \geq \frac{\Delta\sigma}{E} . \tag{5.7}$$

The maximum strain is typically 2% in PF_6^- doped polypyrrole, and the elastic modulus is 0.8 GPa, suggesting that the peak load at which elastic deformation can be compensated for is 16 MPa. At 20 MPa, the sum of the creep and the elastic deformation reaches 2% after ~ 1 hour, as shown in Figure 5.11. The designer must determine the extent of elastic deformation and creep that is acceptable and the time-scale and cycle life of the actuator. Measured creep and stress-relaxation curves and viscoelastic models will then assist in determining the appropriate upper bounds in actuator stresses.

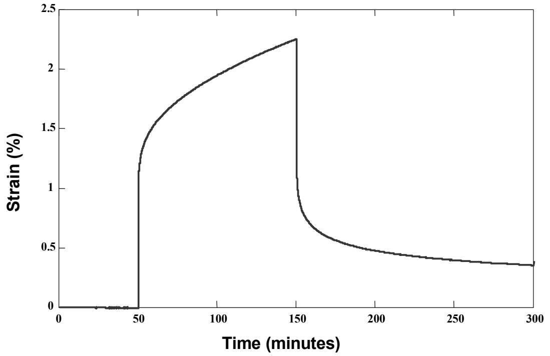


Figure 5.11. Creep in a polypyrrole film in response step in stress (2 MPa to 20 MPa and back to 2 MPa). The test was performed in propylene carbonate with 0.05 M tetraethylammonium hexafluorophosphate

In some designs, the maximum load will be determined by the maximum stress that can be actively generated by the actuator from an unloaded condition, or when acting against another actuator (an antagonist). In such cases, peak stress generated is simply given by the product of the modulus and the active strain:

$$\sigma = E \cdot \varepsilon \tag{5.8}$$

This peak stress will be observed at zero strain. For tetraethylammonium-doped polypyrrole this peak stress is once again 16 MPa.

5.6.3 Actuator Volume

How much space will a conducting polymer actuator consume? Many applications allow only limited volumes. Where a single actuator stroke is used to create motion, as in the action of the biceps muscle to displace the forearm or of a hydraulic piston on a backhoe, the amount of work performed per stroke and per unit volume, u, is a key figure of merit. The actuator volume required, $Vol_{\min}$, is determined based on the work , W, required per cycle:

$$Vol_{\min} \geq \frac{W}{u} \tag{5.9}$$

This volume is the minimum required because energy delivery, sensors, linkages, and often means of mechanical amplification generally also need to be incorporated.

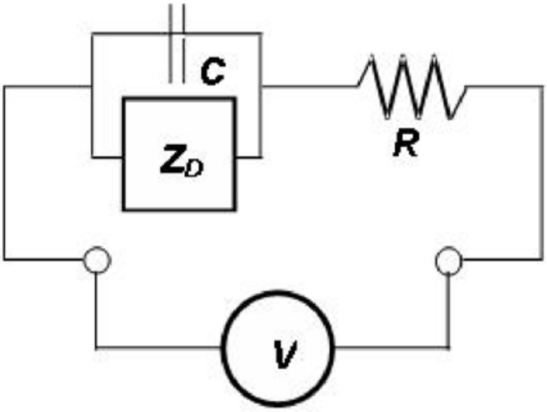


Figure 5.12. Equivalent circuit model of the actuator impedance. V represents an external voltage source, C is the double layer capacitance, R is the electrolyte/contact resistance, and Z_D is the diffusion impedance. © Proceedings of SPIE, reprinted with permission [18]

Work per unit volume is the integral of stress times incremental strain. The maximum stress against which mammalian skeletal muscle can maintain position is

350 kPa and typical strain at no load is 20% *in vivo* [61]. The achievable strain in muscle decreases with increasing stress, the work density is less than 70 kJ·m^{-3}, the product of the peak stress and strain, and in general will be in the range [85] of 8–40 kJ·m^{-3}. Work densities of 70 kJ·m^{-3} have been reported in polypyrrole [72] and exceed 100 kJ·m^{-3} in new, large strain polypyrrole [68]. Note that unlike muscle, conducting polymers can perform work both under compression and tension, and therefore can generate a further doubling in work per volume where this property is used.

5.6.4 Rate and Power

Generally, in any given application, a certain rate of response or output power is required. This section is dedicated to presenting a number of factors that determine the rate of response and estimating how rate will be a function of geometry in such cases. Other factors affecting rate are polymer and electrolyte conductivities, diffusion coefficients, and capacitance. The equations presented enable the designer to determine the physical and geometrical constraints necessary to achieve the desired performance.

As discussed, conducting polymers respond electrically as batteries or supercapacitors with enormous quantities of charge stored per unit volume. The capacitance can exceed 100 F/g [22]. Given that strain is proportional to charge, high strain rates and powers require high currents. Although other factors could also limit rate, including inertial effects and drag, the generally moderate to low rates of actuation in conducting polymers to date suggest that such situations are unusual.

The factors that limit current in conducting polymer actuators are the same as those that limit the discharging rate in batteries and supercapacitors. Internal resistance is one factor. To charge and discharge a battery, the time limit due to internal resistance is the product of the total amount of charge multiplied by the resistance and divided by the voltage. In a capacitor, the time constant is determined by the product of the internal resistance and the capacitance. The two are essentially equivalent because the capacitance is the ratio of the charge and the voltage. The second major limiting factor that will be discussed is the rate of transport of ions into the polymer. Another factor that could also limit response time is the rate at which electrons are exchanged between the conducting polymer and the contacting metal electrode (kinetics). This will not be discussed because it is considered not to be a significant factor, providing that the conducting polymer is in a relatively highly conducting state. More complex effects than those discussed here can also arise due to changes in ionic and electronic conductivity as a function of voltage, which often lead to the advancing of sharp fronts of oxidation state through the material rather than a concentration gradient observed in diffusionlike behavior. Models for these effects are being evaluated and are likely important when the oxidation state of the polymer is brought substantially down toward the completely reduced state [21, 86]. Mechanical relaxation and solvent swelling may also be important [21]. These cases will not be covered here.

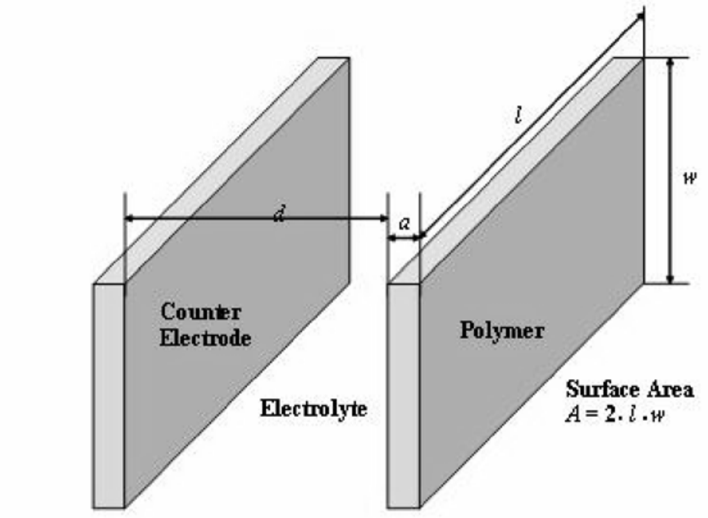


Figure 5.13. Dimensions of the polymer actuator. Electrical contact to the polymer is made at intervals of length *l*. © Proceedings of SPIE, reprinted with permission [18]

Current and potential are related via impedance or its inverse, admittance. Figure 5.12 is an impedance model from which rate-limiting time constants are derived. *R* represents the electrolyte resistance, *C* is the double layer capacitance at the interface between the polymer and the electrolyte [87], and Z_D is a diffusion element, modeling mass transport into the polymer. For planar geometry, as in Figure 5.13, Z_D is expressed in the Laplace or frequency domain as:

$$Z_D(s) = \frac{\delta}{\sqrt{D} \cdot C \cdot \sqrt{s}} \cdot \coth\left(\frac{a}{2} \cdot \sqrt{\frac{s}{D}}\right) \tag{5.10}$$

D is the diffusion coefficient, δ is the double layer thickness, *C* is the double layer capacitance, and *a* is the polymer film thickness. At low frequency (lim $s \rightarrow 0$), the diffusion impedance reduces to

$$Z_D = \frac{\delta}{a \cdot C \cdot s} = \frac{1}{C_V \cdot Vol \cdot s} \tag{5.11}$$

behaving as a capacitance. The right-hand expression restates the impedance in terms of the polymer capacitance per unit volume, C_V, and the polymer volume, *Vol*. Details of the derivation, assumptions, and physical significance of the variables are provided elsewhere [12,19]. In essence it assumes that the rate is determined by either RC charging or the time it takes for ions to go through the polymer. It also assumes that ionic mobiility or the diffusion coefficient does not change significantly over the range of potentials employed and that the electrical conducitivity within the polymer is sufficiently high to eliminate any potential drop. A time constant accounting for potential drop along the polymer due to finite electrical conductivity is discussed below.

The model provides a reasonable description of hexafluorophosphate-doped polypyrrole impedance over a 2 V range at frequencies between 100 μHz and 100 kHz [19,22]. It also suggests the rate-limiting factors for charging and actuation. One is the rate at which the double layer capacitance charges, which is limited by the internal resistance, *R*. A second is the rate of charging of the volumetric capacitor, which is determined by the slower of the rate of diffusion of ions through the thickness and the $R{\cdot}C_V{\cdot}Vol$ charging time. These time constants and their implications are discussed further below.

The impedance model represented in Figure 5.12 is very general in the sense that the time constants derived from it are present in all conducting polymer systems. As a result, it provides a good basis for describing all systems. A more general model will require the addition of finite and changing electronic and ionic conductivities, kinetics effects, and material anisotropies.

Ion transport within the polymer can be the result of diffusion or convection through pores, molecular diffusion, or field-induced migration along pores [13,22,76,77,79–81,88,89]. The mass transport model described by Eq. (5.10) appears to represent only a diffusion response. Eq. (5.10) mathematically describes all of these effects, not just diffusion. The equivalent circuit for the diffusion element is shown in Figure 5.14. It is identical to the equivalent circuit used to describe migration and convection and thus these effects are indistinguishable based on the form of the frequency response alone. It is quite likely that the diffusionlike response is due to a combination of internal resistance (ionic or electronic) and internal capacitance.

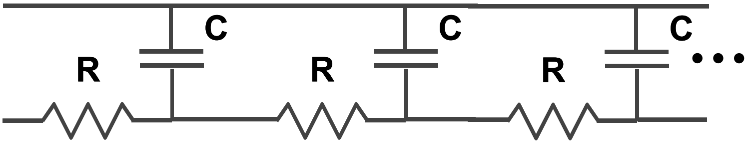


Figure 5.14. Diffusionlike response represented by a transmission line model. The resistors may represent solution resistance, or fluid drag, and the capacitors double layer charging or electrolyte storage. This model also represents the charging of a polymer film whose resistance is significant compared to that of the adjacent electrolyte. In this case, the resistance is that of the polymer, and the capacitance is the double layer capacitance or the volumetric capacitance. © Proceedings of SPIE, reprinted with permission [18]

5.6.4.1 Polymer Charging Time

In conducting polymers, charging occurs throughout the volume. Independent of the nature of the charge-voltage relationship (*e.g.,* battery or capacitor), the charge density is delivered through an internal resistance. There are two primary sources of resistance – the electrolyte and the polymer. To minimize electrolyte resistance, the electrolyte ideally covers the polymer surface area on both sides, $A = 2{\cdot}l{\cdot}w$, with as small an electrode separation, *d*, as possible (refer to Figure 5.13 for dimensions). In a liquid electrolyte, the conductivity, σ_e, can be a high as 1 to

10 S·m^{-1}. For capacitorlike behavior, as in hexafluorophosphate-doped polypyrrole, the time constant for volumetric charging, τ_{RCV}, is

$$\tau_{RCV} = R \cdot C_V \cdot Vol = \frac{d \cdot a}{2 \cdot \sigma_e} \cdot C_V , \tag{5.12}$$

where electrolyte resistance is large compared to the polymer resistance. To charge a 10 μm thick film in 1 s and given an electrolyte conductivity of 10 S·m^{-1}, the electrolyte dimension, d, must be less than 20 mm.

The polymer resistance can dominate RC charging time in long films, poorly conductive polymers, or over a range of potentials where the conducting polymer is no longer in its quasi-metallic state. In such a case, the combination of the film resistance and the volumetric capacitance forms a transmission line, as depicted in Figure 5.14, with the polymer resistance along the length of the film. The charging time constant can be reexpressed in terms of the polymer conductivity, σ_p, and the film length, l:

$$\tau_{RCVP} = R_p \cdot C_V = \frac{l^2}{4 \cdot \sigma_p} \cdot C_V \cdot \tag{5.13}$$

The factor of 4 is appropriate only when both ends of the film are electrically connected. If the electrical connection is only from one end, the four is replaced by one. A 20 mm long film having a conductivity of 10^4 S·m^{-1} (typical of hexafluorophosphate-doped polypyrrole) has a time constant τ_{RCVP} = 1 s.

The keys to improving R·C response times are to reduce the distance, l, between contacts, the distance between electrodes, d, and the polymer thickness, a. Maximizing electrolyte and polymer conductivities is also important. Finally, if the volumetric capacitance can be reduced without diminishing strain, the charge transfer is reduced. New polymers are being designed and tested whose strain to charge ratio is much larger and capacitance is lower [90]. These polymers promise to charge faster while also developing greater strain, compared to polypyrrole.

5.6.4.2 Resistance Compensation

Higher current in a circuit can generally be achieved by applying higher voltage. However, extreme voltages applied to the polymer lead to degradation. There is a simple case in which the application of a high voltage for a short amount of time will lead to faster actuation without degradation. If the solution resistance (and any contact resistance) is large compared to the polymer resistance, then immediately after the application of a step in potential, nearly all the potential will be across this series resistance. This is essentially the same as a series RC circuit, in which initially all the potential drop is across the resistor. At long times, as in the series RC circuit, all potential drop is across the capacitor. If we can prevent the resistance across the polymer from exceeding a threshold value, then we can avoid degradation while having increased the initial rate of charging and hence the actuation rate [19].

The polymer diffusion impedance, Z_D, and double layer capacitance, C, in Figure 5.12, act as a low-pass filter. The electrolyte resistance is then easily identified (*e.g.*, using a step, impulse, or high-frequency sinusoidal input). The product of the current and the resistance, $I \cdot R$, is the drop across the electrolyte. Subtracting this voltage from the total applied potential, V, provides an estimate of the double layer potential, V_{dl}. If the double layer potential should reach but not exceed a voltage, $V_{\mathrm{dl}}^{\max}$, then the controller must simply maintain the input voltage such that the applied potential V:

$$V \leq V_{dl}^{\max} + I \cdot R \,. \tag{5.14}$$

This method effectively eliminates the rate-limiting effects of the resistance, R, in Figure 5.12 [42,91]. The remaining rate-limiting factors are then due to polymer resistance and mass transport, which are now discussed. The method does not work if polymer resistance is similar in magnitude or larger than the cell resistance.

5.6.4.3 Mass Transport

Ions move in the polymer to balance charge during oxidation and reduction. This can occur by molecular diffusion [19,22], conduction, or diffusion through electrolyte filled pores [76,77,79–81,88,89] and convection through pores [13]. The mathethematical form of the solutions is represented by Equation (5.10). The mass transport related charging time constant is

$$\tau_D = \frac{a^2}{4 \cdot D}, \tag{5.15}$$

where D is the effective diffusion coefficient and a is the film thickness. The factor of 4 is removed if ions have access only from one side of the film. Diffusion coefficients in hexafluorophosphate-doped polypyrrole appear to range[19,22] between 0.7 and 7×10^{-12} $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$. To obtain a 1 s response time, the polymer film thickness must be less than approximately 5 μm.

5.6.5 Summary of Rate-Limiting Effects

Volumetric charging times, (τ_{RCV} and τ_{RCVP}) and diffusion time (τ_D) are key rate-limiting factors that can be minimized by reducing the distance between electrodes, d, the spacing between contacts, l, and the film thickness, a. Reduction in film thickness and length are particularly effective because diffusion time and volumetric charging time are proportional to the squares of these lengths.

How fast could a conducting polymer film actuate? A 10 nm thick polypyrrole actuator that is several micrometers long is predicted to exhibit a diffusion time constant of 3 μs. Charge and discharge curves from similarly thin electrochemically driven transistors and electrochromic devices approach such a rate [26, 58]. The need for small dimensions to achieve fast response suggests that conducting polymer actuators are well suited for micro- and nanoscale applications. The next section takes a general look at what applications and scales are currently attractive for conducting polymer actuators.

5.7 Opportunities for Polypyrrole Actuators

Established actuator technologies used in robotics [92] for which artificial muscle technologies might offer an alternative include internal combustion engines, high-revving electric motors, direct drive electric motors, and piezoelectric actuators. Conducting polymers are not ready to compete with the internal combustion engine and high-revving electric motors in high power propulsion systems. They are appropriate for intermittent or aperiodic applications with moderate cycle life requirements and could replace solenoids, direct drive electric motors, and some applications of piezoceramics. This section follows the format of the introduction in a paper on the application of polypyrrole in variable camber foils [93] which seeks to answer the general question where conducting polymer actuators are useful. The challenges in creating large, high power actuators based on conducting polymers are then discussed in Section 5.8 using the example of a simulated biceps muscle.

5.7.1 Propulsion

The internal combustion engine with its 1000 W/kg power and fuel energy of ~43 MJ/kg is hard to beat for high-speed propulsion of automobiles and ships. Electric motors achieve specific power similar to the internal combustion engine and efficiencies of >90% [92]. Fuel cells and hybrid engines provide energy sources that make such high revving electric motors feasible. Of the available actuator technologies, only shape-memory alloys and piezoceramic actuators clearly surpass the power to mass of internal combustion engines and electric motors [61], but there are efficiency and cycle life issues with shape-memory alloys and mechanical amplification challenges with piezoelectrics. Can conducting polymers offer any advantages in propulsion?

The power densities of conducting polymers and carbon nanotubes are within a factor of four of the combustion engine [94]. Their musclelike nature may make polymers and nanotubes more suitable for biomimetic propulsion – such as robot walking, swimming, or flying. However, the low electromechanical coupling of conducting polymers (ratio of mechanical work output to electrical energy input) means that either the efficiency will be low, or additional energy recovery circuitry will be required. No polymer-based actuator technology has yet demonstrated cycle lifetimes [90] of more than 10^7 and thus lifetime is generally not long enough for sustained propulsion. For example, continuous operation at 10 Hz may lead to failure after 10 days or less. Conducting polymer and other novel polymer actuators do not yet offer compelling alternatives to electric motors and combustion engines for high power, continuous propulsion.

5.7.2 Intermittent Actuation

Motions such as the grasping of parts by a robot arm, the opening of a valve, and the adjustment of a hydrodynamic control surface are difficult to perform using high revving electric motors and combustion engines. Direct drive electric motors are often used instead. Direct drive motors suffer from relatively low torque and force. Honda's elegant servomotor driven Asimo, for example, is limited in walking speed to ~ 2 km/hr due to the low torque of its muscles (http://world.honda.com/ASIMO/P3/spec/). Also electromagnetic actuators expend energy to hold a force even without displacement, wasting energy. Conducting polymers expend minimal energy while holding a force, feature high work density, and produce high stresses and strains, making them well suited for discontinuous, aperiodic tasks such as the motion of a robotic arm or the movement of a fin [85]. Some challenges are encountered in using the current properties of conducting polymers for moderate to large scale applications, as explained in the next section.

5.8 Challenges in Fabrication and Energy Delivery: Example – Biceps Muscle

To contract quickly, conducting polymer actuators need to be thin. They also have relatively low electromechanical coupling. Low electromechanical coupling does not necessarily mean low efficiency, as energy can be recovered from conducting polymers due to their capacitive nature. However, it does imply that a much larger amount of electrical energy needs to be transferred to the polymer than the amount of work performed, this energy then is either dissipated or recovered. Conducting polymer actuators operate at low voltages and the coupling is low, the implication is that currents will be very high in large, high power devices. Thin films and relatively large currents are less of a concern in micro and nano devices where dimensions are small, heat transfer is good, and batteries are readily available. However in scaling up even to moderate size, the challenge can be considerable, as made clear in the example of creating a biceps muscle.

The biceps muscle does about 45 J of work in one stroke [18]. Using Eq. (5.9) relating work and work density to the minimum actuator volume and assuming a work density of about 100 kJ/m^3, the volume of conducting polymer required to produce this work is approximately 500 ml. For the contraction to occur in one second, then based on Eq. (5.15), the polymer thickness must be about 5 μm. Assuming a biceps length of 150 mm and a square cross section that is 55 mm across, 11,000 layers of conducting polymer are needed to achieve the desired speed. Equation (5.12) predicts that the counterelectrode must be placed within 40 mm of the working electrode, and thus will have to be integrated with it. Equation (5.13) suggests that the electrical contacts to the polymer must be spaced by less than 20 mm. The need for the multiple thin layers and separators suggests a considerable fabrication challenge. This may be eased by using porous polymers in which mass transport is enhanced by allowing ions to travel into the polymer via liquid filled capillaries [59]. Nevertheless the challenge is significant.

The current needed to charge a conducting polymer bicep is substantial. Assuming a capacitance of 130 farads per ml (based on 100 F/g), it will take about 65 000 C, which needs to be delivered within 1 second. Normally such huge currents would be unthinkable. Fortunately, beacuse conducting polymers act as energy storage devices, enough energy for one cycle can be stored in the counter-electrode (which likely will also be polymer, and act as the antagonistic muscle – *e.g.*, triceps). 90% or more of the input energy is recoverable [19,22], a combination of batteries and capacitors can be used to store the additional 10 % of energy needed for each cycle. The fabrication and control are not trivial, however.

As the size scales down, the currents also drop dramatically. For example, a 1 mm^3 actuator needs only about 130 mA of current. At present, moderate to small size actuator applications are the most promising for conducting polymer actuators. Larger devices require substantial attention to the details of design and fabrication. New materials are being developed [63,95] which promise to dramatically increase electromechanical coupling and reduce the amount of charge transferred, easing scaling issues [90].

5.9 Summary of Properties

The chapter has described the current state of synthesis, modeling, application, and analysis of polypyrrole actuators. Polypyrrole and other conducting polymer actuators are evolving rapidly, with strains increasing dramatically over the past two years alone, for example [96,97]. It is likely that further improvments will be made in cycle life [98] and possibly also in load bearing capacity. Currently, the advantages and limitations of polypyrrole actuators are

Limitations:

Mass transport of ions and the high capacitance limits rates of actuation; high rates are several hertz, though these can potentially reach kilohertz frequencies using microstructured electrodes.

Low electromechanical coupling and low voltage operation mean that very high currents are needed to drive large actuators at moderate speeds, making scaling a challenge. In principle, high currents can be delivered by polymer supercapacitors, solving the problem.

Cycle life is still only moderate, limiting the range of applications unless regeneration or replacement strategies can be used.

If a liquid electrolyte is to be used, some encapsulation is often required.

Advantages:

Low voltage operation (several volts),
Low cost, flexible materials,
High work density (~100 kJ/m^3),
Moderate stress (1–5 MPa typical),
Moderate to high strain (2 – >20%),
Catch state (no work expended to hold a load),

Miniature devices are expected to be fast,

Versatile materials from which electronics, energy storage, structural elements, sensors as well as actuators can all be constructed.

5.10 Acknowledgment

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